Advances in Polyurethane Dispersions

2021 Coatings Trends and Technologies
Lombard, IL
September 8, 2021

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Outline

Introduction
  History
  Chemistry and Morphology
  PUD manufacturing

Properties of Polyurethane Dispersions

Innovative Technologies

Applications

Conclusions
Introduction: PU History and Morphology

- Otto Bayer invented PU
  - Isocyanate/PUs
  - Urethane lacquers

1930

1940s

- Rigid PU foams
- Isocyanate/alkyds
- Urethane elastomers
- Aromatic prepolymer in coatings

1950s

- Flexible PU foam
- Polysocyanate alkyd enamels

1960s

- Polyisocyanate alkyd enamels

1970s

- PUDs
- 2-component PUs
- 1-K Blocked Iso systems

1980s

- RIM
- 2-K WB PU coatings

1990s

- 2-component PUs
- 1-K Blocked Iso systems

- 2-K WB PU coatings

Soft segment

- Acts as crosslinking point
- Will release under strain
- Allows flow to relieve stress
- Allows self healing of defects

Hard segment

2-100 nm

H-Bonding
Traditional PUD Building Blocks for Coatings

**Isocyanates**

- $H_{12}MDI$
- IPDI
- TMXDI
- HDI

**Polyols/Co-reactants**

- Polyether polyol
- Polyester polyol
- Polycarbonate polyol
Pre-polymer preparation
A polyol is reacted with a stoichiometric excess of isocyanate to produce a pre-polymer. Dimethylpropionic acid (DMPA), an anionic stabilizing agent, is used to build functionality into the polymer chain.

Neutralization
An amine, typically TEA or DMEA, is used for neutralization.

Dispersion
The pre-polymer is dispersed in water.

Chain Extension
Molecular weight is increased.
Traditional PUD Chemistry

OCN-R-NCO + OH-P-OH + HOCH₂-CH₂OH

=C=O + CH₃

(Catalyst)

NMP

Acetone or MEK

Reactive diluent

DMPA

OCN-R-NH-C-O-P-O-C-NH-R-NH-C-O

=O

(O-Polyol)

COOH

COOH

NR₃

OCN-R-NH-C-O-P-O-C-HN-R-NH-C-O

=O

(O-Polyisocyanate)

COOH

COO⁻⁺NHR₃

OCN-R-NH-C-O-P-O-C-NH-R-NH-C-O

=O

(O-Polyol)

COOH

COO⁻⁺NHR₃

NR₄⁺

OH⁻⁺NHR₃

Polyurea/urethane Dispersion

Water/polyamine

50-500 nm
**Dimethyl Propionic acid**
- Typically used with tertiary amines
- Loose hydrophilicity upon amine evaporation
- Relatively high Tg component
- Insoluble in PU component

**Sodium Sulfonate Diols**
- Na salt remains in film
- Relatively low Tg component
- Improved solution stability of polyesters

**Tertiary amine diol**
- Typically used with HCl or AcCOOH
- Commonly used for paper and leather application
Solvent-free PUDs

- Traditional PUDs were manufactured using N-methyl-2-pyrrolidone (NMP) to reduce the pre-polymer viscosity.
- Environmental restrictions against NMP have lead to the development of solvent-free PUDs.
- Distillation - Acetone or MEK is used to control the pre-polymer viscosity. Then after the chain extension the acetone or MEK is removed.
- Reactive diluent – A reactive diluent, such as an acrylic monomer, is used to control the pre-polymer viscosity and then polymerized.
- Innovations in equipment have lead to dispersing units that can handle much higher viscosity materials.
POLYOLS  ISOCYANATES  SOLVENT  DMPA (solid)

POLYOLS  ISOCYANATES

PREPOLYMER REACTOR

H₂O

R₃HN⁺· OOC  ~ CO₂⁻ + NHR₃
Properties of Polyurethane Dispersions

Abrasions Resistance

Flexibility

Scratch and Mar Resistance

Hardness

Toughness

Weatherability

Functionality - Crosslinkable
Crosslinking of PUDs: Common Approaches

Melamine formaldehyde

Polyaziridine

R-N=\overset{\mathcal{\Sigma}}{-}N-R

Carbodiimide

X-(CH_2)_n-Si-(OR)_3

n: \sim 3-5

X: \text{NH}_2, \text{OH, NCO, epoxy}

R: \text{CH}_3, \text{C}_2\text{H}_5, \text{C}_3\text{H}_7

Emulsifiable isocyanate

Functional siloxanes
Innovative Technologies

Renewable PUDs
- Castor Oil
- Linseed Oil

UV Curable PUDs

Amine-free PUDs

Inherently Matte PUDs
Polyurethane Dispersions Based on Renewable Resources

\[
\begin{align*}
R & \quad \text{Isocyanate} \\
+ & \quad \text{Polyol based on natural oils} \\
\rightarrow & \quad \text{Polyurethane Dispersion}
\end{align*}
\]

**Natural oils extracted from:**
- castor beans
- soybeans
- flax seeds
- rapeseeds
Castor Oil

Major component in castor oil, produced via an esterification reaction involving ricinoleic acid.

This fatty acid contains a hydroxyl functionality on the twelfth carbon which allows further chemical modification, specifically reaction with isocyanates to produce polyurethanes.
Polyurethane Dispersions Based on Castor Oil

Used for 1K and 2K Floor Coatings and Furniture Coatings
Excellent abrasion resistance
Outstanding wood warming properties
Excellent black heel mark resistance
Excellent gloss

Used for interior “green” wall paints and hobby adhesives
Very good pigment wetting
Amine-free
Odor and VOC free
Non-yellowing
Conforms to European Toy Regulation EN 71-3
Available with elongation at break values ranging from 60% to 175%

Available with Koenig Pendulum Hardness values ranging from 85 to 115 seconds

Available with a renewable content ranging from 8% to 40%
Alternative to solvent-borne urethanes, suitable for parquet-coatings and DIY-lacquers

Solvent-free

Outstanding wood warming properties

Oxidative drying - faster drying with addition of driers (e.g. Co, Mn for surface drying and Ba, Zr for through drying)

Excellent exterior durability

Alkyd-like flow
Triglyceride found in Linseed Oil, a triester derived from linoleic acid, alpha-linolenic acid, and oleic acid.
Oxidative cure of Linseed Oil based PUDs

\[ M^+, \, O_2 \rightarrow \text{COONHR}_3 \]

\[ \text{X} : \text{C-O, C-C} \]

\[ : \text{-OC(O)NH-R-NHC(O)O-} \]

\[ : \text{Oil Ester with Fatty Acid Chain} \]
Linseed Oil Based PUDs

**Application Areas include:**

- Hardwood floor coatings
- DIY lacquers
- Furniture coatings
- Exterior wood coatings
- Wood stains
Linseed Oil Based PUDs

- Contains 30 - 50% renewable content
- Very fast hardness development
- Excellent adhesion
- Solvent-free formulations are possible
- Excellent chemical resistance
- Very good sanding properties
Emerging Technologies – Other Renewable PUDs

Rapeseed

Soybean
UV Curable PUDs

Very low VOC
No low molecular weight reactive diluents needed
Excellent grain definition
Excellent atomization and flow
Little to no shrinkage
Excellent block resistance
Wide range of application methods
Easy formulating and flattening
Immediate property development
Can be easily formulated to pass KCMA specifications
UV Curable PUDs

- High molecular weight dispersions; lower crosslinking density
  - Low shrinkage
  - Adhesion to multiple substrates
- Excellent chemical resistance
- Excellent mechanical properties
- Multiple polymer design options
- Low MFFT --- Solvent free formulations; no reactive diluent
- Dual cure options
Ultraviolet (UV) curing is a photochemical process where intense UV light is used to cure coating.

Photopolymerization is achieved through a free radical mechanism. A photoinitiator is the “catalyst” for the free radical mechanism.

UV light splits the photoinitiator into free radicals.

The radicals react with the double-bonds of the UV-dispersion.

This produces more free radicals and the reaction process continues until terminated.

By the use of multifunctional resins, a three dimensional network can be created.
A traditional UV PUD stabilized with DMPA/tertiary amine has been compared to a similar UV PUD stabilized with Sodium Sulfonate and evaluated for:

Koenig Pendulum Hardness
Dry Time
Chemical Resistance
Boiling Water Resistance
Scratch Resistance
Elevated Temperature Stability (50°C)
Koenig Pendulum Hardness

Traditional UV PUD
Experimental UV PUD

before cure  after cure
Dry Time

Set to touch (minutes)

- Traditional UV PUD
- Experimental UV PUD
Chemical Resistance  16-hour spot test

- 100 proof alcohol
- mustard
- coffee
- IPA (70%)
- ammonia
- acetone

Traditional UV PUD
Experimental UV PUD
Scotch Brite Scratch Resistance - % Gloss Loss

- Traditional UV PUD
- Experimental UV PUD

The graph shows a comparison between Traditional UV PUD and Experimental UV PUD in terms of Scotch Brite Scratch Resistance, measured in % Gloss Loss.
## Elevated Temperature Stability – 50°C

<table>
<thead>
<tr>
<th></th>
<th>Traditional UV PUD</th>
<th>Experimental UV PUD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial Viscosity (cps)</td>
<td>142.5</td>
<td>16</td>
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<tr>
<td>Viscosity after 7 days</td>
<td>130.1</td>
<td>16</td>
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<tr>
<td>Viscosity after 14 days</td>
<td>68.5</td>
<td>17.5</td>
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<td>Viscosity after 21 days</td>
<td>2360</td>
<td>15.5</td>
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<tr>
<td>Viscosity after 30 days</td>
<td>gelled</td>
<td>16</td>
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</table>

<table>
<thead>
<tr>
<th></th>
<th>Traditional UV PUD</th>
<th>Experimental UV PUD</th>
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<tr>
<td>Initial pH</td>
<td>6.99</td>
<td>6.92</td>
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<tr>
<td>pH after 7 days</td>
<td>6.51</td>
<td>6.93</td>
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<tr>
<td>pH after 14 days</td>
<td>6.06</td>
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<td>pH after 21 days</td>
<td>5.54</td>
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<tr>
<td>pH after 30 days</td>
<td>gelled</td>
<td>6.26</td>
</tr>
</tbody>
</table>
Conclusions

The experimental UV PUD has equal performance to the traditional UV PUD but has superior elevated temperature stability.
Amine-free PUDs

- Uses ammonia as neutralizing agent
- High surface hardness
- Very good chemical resistance
- Suitable for wood floor and furniture coatings
- Ideal for crosslinking with carbodiimides and silanes. The use of polyisocyanate is not recommended due to very high reactivity.
Amine-free PUDs
Background: The case for amine free

• Triethyl amine (TEA) is the most common neutralization agent for PUDs.

• According to GHS labeling it is flammable, harmful and toxic to the skin and eyes.

• Due to this classification, resulting binders and paints with TEA >1% have classification:

• TEA has a significant impact on emissions and indoor air quality.
An amine-free PUD has been evaluated for use in KCMA/Furniture applications. Performance has been benchmarked against a traditional PUD and evaluated for:

- Chemical resistance
- Boiling water resistance – 1 hour
- Scrape adhesion
- Taber Abrasion
- Edge soak
- Wood Tone
- Block resistance
Chemical/Stain Resistance – 16 hour spot test

Traditional PUD

Amine-free PUD

Ethanol (50%)  Coffee  Red Wine
Mustard Resistance – 1 hour spot test

Traditional PUD

Amine-free PUD

Initial  After recovery
NEMA Boiling Water Resistance

Traditional PUD

Amine-free PUD
BYK Balanced Beam Scrape Adhesion and Mar Tester – 5 Kg

Traditional PUD vs. Amine-free PUD
Edge Soak

Application:

Spray sealer coat @ 4 – 5 wet mils on solid red oak; air dry 1 hour and sand; spray topcoat at 4 – 5 wet mils; air dry 15 minutes; force dry 15 minutes at 50C; age 7 days. Place finished end grain area on sponge soaked in 1% detergent solution for 16 hours. Allow to recover for 4 – 8 hours. Examine for blushing and cracking.
Taber Abrasion Resistance – 1000 grams; 1000 cycles; CS 17 wheels

Application:

6.0 Bird draw down on black scrub paper; air dry.

Age 7 days to test.
Conclusions

The amine-free PUD has excellent ethanol, Taber abrasion and water resistance.

It has excellent wood warmth and it atomizes and builds well.

The amine-free PUD is an excellent candidate for a KCMA and/or furniture coating.
Inherently Matte PUDs

- High optical clarity on dark surfaces
- Hard but flexible film
- Anti-slip properties
- Excellent sandability
- Very good chemical resistance
- Very good blocking resistance
Particle size and particle shape can be controlled which influences haptic properties and gloss level.
Matting efficiency vs. pyrogenic silica in traditional PUD

![Graph showing the matting efficiency of different compositions.]

- **10% Inherently matte PUD**
- **0.5% pyrogenic silica**
- **60% Inherently matte PUD**
- **1.5% pyrogenic silica**
- **100% Inherently matte PUD**

Gloss units measured at 20°, 60°, and 85°.
Gloss After Scrubbing – Burnish Resistance

![Graph showing Gloss After Scrubbing for different coatings.](image)
Applications for Polyurethane Dispersions

- Kitchen Cabinets and Office Furniture Coatings
- Hardwood Floor Coatings
- Exterior Wood Coatings
- Textile and Leather Coatings
- Architectural Wall Paints
Industrial Spray Lines (Cabinetry)
Polyurethanes are the dominant choice for wood floors due to their flexibility, toughness and chemical resistance.

Solvent-based (1K oil modified) and Water-based (1K & 2K) materials are available in the market.

The Maple Flooring Manufacturer’s Association (MFMA) is the authoritative source of technical and general information about maple flooring and related sports flooring systems.
Several PUD types have been evaluated as 1K floor coatings according to the testing protocol of the MFMA.

PUDs Evaluated:
- NMP Containing PUD
- Solvent-free PUD
- Linseed Oil Based PUD
- UV PUD
- Acrylic PUD Copolymer
- Amine-free PUD

Performance Criteria:
- Gloss
- Hardness
- Black Heel Mark Resistance
- Chemical Resistance
- Taber Abrasion
- Coefficient of Friction (CoF)
Gloss
Koenig Hardness Development

![Bar chart showing hardness development over time for different types of PUDs: NMP-PUD, SF-PUD, LO-PUD, UV-PUD, UAc-PUD, and AF-PUD. The chart compares hardness at 1 day, 3 days, and 7 days.]
Taber Abrasion

mg loss

<table>
<thead>
<tr>
<th></th>
<th>NMP-PUD</th>
<th>SF-PUD</th>
<th>LO-PUD</th>
<th>UV-PUD</th>
<th>UAc-PUD</th>
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<td>Loss</td>
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<td>-10</td>
<td>-15</td>
<td>-20</td>
<td>-25</td>
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Black Heel Mark Resistance

3 days
7 days

NMP  SF  UAc  AF  LO  UV
## Chemical/Stain Resistance (1h spot test)

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<tr>
<th></th>
<th>NMP</th>
<th>SF</th>
<th>UAc</th>
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<td>Red wine</td>
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<td>3</td>
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<td>Deonized water</td>
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<td>Mustard</td>
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<td>Olive oil</td>
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<td>70 % IPA</td>
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<tr>
<td><strong>Rating:</strong> 0 – 5; 5 = best</td>
<td>76</td>
<td>77</td>
<td>76</td>
<td>75</td>
<td>74</td>
<td>85</td>
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</table>
Conclusions

All formulations resulted in high gloss coatings.

The UV PUD had the highest hardness values followed closely by the linseed oil-based PUD.

Taber abrasion of all coatings was excellent.

Black heel mark resistance was very good in all coatings except the amine-free product.

Chemical resistance was good in all coatings with the UV PUD being superior.
PUDs for Flexible Substrates – Textile and Leather Coatings

Features:
- Extreme Flexibility
- Hydrolysis Resistance
- Non-Yellowing
- Cold Resistance
- Chemical Resistance
- Light Fastness
- Abrasion Resistance

Recommended Applications:
- Automotive Leather
- Automotive Interior Plastics
- Synthetic Leather
- Textile Coatings
Conclusions

• PUDs are one of the dominant resin technologies used to coat multiple substrates.

• Advances in PUD technology have resulted in a wide range of compositions offering unique performance to meet application requirements.

• PUDs can be blended with other waterborne technologies (acrylcs, alkyds...) to enhance performance.

• PUDs are viable alternatives to traditional solvent-borne coatings.
Questions?

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